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Electrochemical oxygenation of diorganyldichlorosilanes: a novel route to generation of diorganylsilanones

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Abstract

Interaction of diorganyldichlorosilanes R_2SiCl_2 (R = Me, Et, Ph) with superoxide or peroxide anions, produced in situ by electroreduction of molecular oxygen, provides short-living diorganylsilanones $R_2Si{=}O$. The latter undergo cyclization to give lower perorganylcyclosiloxanes $(R_2SiO)_n$, $n = 3$ or 4 and then insert to the molecules of these primary products to form higher cyclic oligomers. When the process is carried out in the presence of a reagent-trap for silanones (hexamethyldisiloxane, hexamethylcyclotrisiloxane), the products of insertion of diorganylsilanones into the molecule-traps $(Me_3Si(OSiR_2)_nOSiMe_3$ with $n \geq 1$, and $(Me_2SiO)_3(R_2SiO)_m$ with $m \geq 1$, respectively) were obtained.

Keywords: Diorganylsilanones; Dialkyldichlorosilanes; Diaryldichlorosilanes; Superoxide anion; Electrosynthesis

1. Introduction

Silanones, very labile compounds of silicon, are key intermediates in the reactions of silicon organic compounds containing a Si–O siloxane bond [1–10]. As individual compounds, diorganylsilanones $R_2Si{=}O$ were only observed in a Ne or Ar matrix when their IR spectra were registered [4–6,8]. These compounds are of great theoretical (as compounds of a three-coordinated silicon with a double bond silicon–element) and practical (as precursors of various siloxane structures) interest as well.

Reactions in which the formation of diorganylsilanones is practically undoubted, are processes of thermal (400–800°C) [11–20] or photochemical [1–10,21–23] destruction of many silicon organic compounds containing the Si–O bond. During recent years, Voronkov developed a conception, according to which silanones are generally produced as a result of a geminal cleavage (the α-elimination) of organic compounds containing a Si(OR)X group [9,10,24] as depicted by the following scheme:

$$>Si(OR)X \rightarrow >Si{=}O + RX \quad (1)$$

Many low-energetic processes, involving silanones as intermediates, occur according to this scheme at reasonably low temperatures [9,10]. In particular, there are reactions of diorganyldichlorosilanes with DMSO [24–27], with metal oxides [24], with salts of several oxygen-containing acids [28], and also the hydrolysis of R_2SiCl_2 under specific conditions [29]. In these reactions, the formation of diorganylsilanones was proven by using 'traps' (specific reagents able to intercept silanones), e.g. hexamethyldisiloxane. Diorganylsilanones have also been shown to be intermediate products in the reactions of oxidation of silenes and silylenes by some oxygen-containing compounds (DMSO, ketones, epoxydes) [3,30–32], as well as during the photolysis of linear [33] and cyclic perorganyloligosilanes [34] in DMSO. Corresponding silanones were formed in a matrix by the oxidation of hydrosilanes of the formula $Me_{4-n}SiH_n$ ($n = 2$, 4) with either oxygen or ozone at 10–15 K [35–38].

The intermediacy of $Cl_2Si{=}O$ was used to explain the formation of linear and cyclic perchlorosiloxanes in the reaction of $SiCl_4$ with oxygen at 1000°C [39]. The formation of diorganylsilanones was reported during

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